Self-Cleaning Boudouard Reactor for Full Oxygen Recovery from Carbon Dioxide

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Oxygen recovery from respiratory carbon dioxide is an important aspect of human spaceflight. Methods exist to sequester the carbon dioxide, but production of oxygen needs further development. The current International Space Station Carbon Dioxide Reduction System (CRS) uses the Sabatier reaction to produce water (and ultimately breathing air). Oxygen recovery is limited to 50% because half of the hydrogen used in the Sabatier reactor is lost as methane which is vented overboard. The Bosch reaction, which converts carbon dioxide to oxygen and solid carbon, is capable of recovering all the oxygen from carbon dioxide, and it is a promising alternative to the Sabatier reaction. However, the last reaction in the cycle, the Boudouard reaction, produces solid carbon, and the resulting carbon buildup eventually fouls the catalyst, reducing reactor life and increasing consumables. To minimize this fouling and increase efficiency, a number of self-cleaning catalyst designs have been created. This paper will describe recent results evaluating one of the designs.

Nomenclature

CRS	=	carbon dioxide reduction system
cc	=	cubic centimeters
g	=	grams
GC	=	Gas Chromatograph
h	=	hours
MF	=	molar flow rate
VF	=	Volume flow rate
sccm	=	standard cubic centimeters per minute

I. Introduction

OXYGEN recovery from respiratory carbon dioxide, CO_2, is an essential aspect of human spaceflight and Mars exploration. Methods exist to capture the CO_2, but production of oxygen, O_2, needs further development. The current ISS Carbon Dioxide Reduction System (CRS) uses the Sabatier reaction to produce water, H_2O, which is electrolyzed to make O_2 for breathing air. O_2 recovery is limited to 50% because half of the hydrogen, H_2, used is lost

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as methane, CH_4, which is vented overboard, and supplemental H_2 availability is limited. The Bosch reaction, Equation 1, is a promising alternative to the Sabatier reaction that does not consume H_2 (the water produced is electrolyzed to make the oxygen product and H_2, which is recycled). The Bosch reaction can be considered to be the combination of the Reverse Water Gas Shift (RWGS) reaction and the Boudouard reaction, as shown in Figure 1. However, during the Boudouard reaction step the resulting carbon buildup eventually fouls the catalyst, reducing reactor life and increasing the use of consumables. NASA has been investigating the Bosch reaction for spacecraft oxygen recovery for many years. An early study developed a Bosch system with catalyst cartridges that could be replaced when they were fouled.[1] More recently, Abney et al.[2–7] have investigated different configurations and catalysts. They demonstrated full conversion of CO_2 into O_2 and carbon using the Bosch reaction with a steel wool Boudouard catalyst using only 0.0019 g of catalyst/g O_2 recovered and showed that other catalysts can improve the kinetics and the capacity to hold carbon before failing. Nevertheless, the catalyst bed is eventually clogged with carbon, and the catalyst is not recoverable.

$$CO_2 + 2H_2 \rightarrow C + 2H_2O \quad (1)$$

To minimize this fouling, find a use for this waste product, and increase efficiency, we have designed various mechanical cleaning methods for catalysts and selected a few which we deem the most reliable for conversion and fouling resistance. Criteria that we considered include the estimated mechanical reliability of the cleaning method and its ability to maintain high conversion efficiency. The chemical reactions of the Bosch process are well understood, but reusable self-cleaning Boudouard catalysts are still needed.

As noted above, the current ISS O_2 recovery method utilizes the Sabatier process which is only 50% efficient due to limits on H_2 availability. The source of the H_2 is the electrolysis of water launched from the ground to make O_2. This means that for a full crew over 3 kg of H_2O/day are used in making O_2 that is not recovered from CO_2. At cargo launch prices of $10,000-$40,000/kg, this costs $30,000-$120,000/day depending on the supplier. For deep space exploration missions, in-space resupply is virtually impossible, so nearly 100% recovery is essential to reduce launch mass. In addition, the carbon product could be used as air or H_2O purification filters which we plan to test, as a filler for 3D printing, as a dry lubricant suitable for low-pressure applications, or as a reactant in other processes such as carbothermal reduction or as consumable electrodes for metal production. By producing a self-cleaning Boudouard reactor the single greatest challenge of the Bosch process is resolved and full O_2 recovery can be realized. The decrease in consumable requirements will be significant for the ISS and enabling for deep space exploration missions.

In this paper, results from a novel self-cleaning Boudouard reactor are presented. Yields, carbon collection efficiencies, and lifetime of the reactor will be presented. A total of ten different reactor designs were conceived during this project, including spring-based, brush-based, and ball bearing-based systems. Actuation methods included purely mechanical (motor-driven) and magnetic actuation systems. The top candidate reactor design concept was down-selected based on several factors, including ease of fabrication, likelihood of success for cleaning, and robustness. The top candidate chosen was the rotating brush reactor design concept. This design was chosen primarily due to the expected ease of fabrication, overall durability and large catalyst area. Additionally, this design provides an opportunity to create several variations of the design by simply changing the rods and brush materials allowing for flexibility during the testing process.

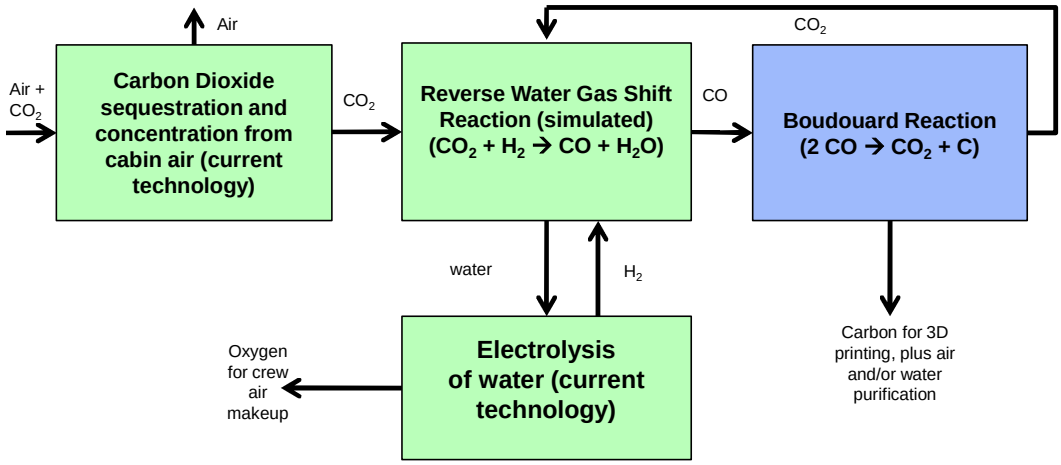

Figure 1. Schematic Representation of the Bosch Reaction by a Combination of the RWGS Reaction and the Boudouard Reaction Followed by Electrolysis of Water to Recover Oxygen from Carbon Dioxide.

II. Materials and Methods

A. Boudouard Reactor Tests

Two reactors with the same self-cleaning mechanism but with 1-inch or 2-inch diameters have been evaluated. In this design, carbon forms on the catalytic brush and is removed by making contact with non-catalytic rods located along the sides of the reactor. The rods are inserted as a unit, with support rings along the rods and a funnel at the bottom to help in carbon removal, as shown in Figure 2 center. Figure 3 shows pictures of the brush inside the rods and the entire apparatus inside a clear PVC tube to show the configuration inside the reactor.

The fabricated reactors (1- and 2-inch diameter) utilize 18-inch long threaded stainless steel pipe nipples as the reactor bodies. Threaded 6-inch diameter stainless steel flanges are attached to each end of the reactor body. A 4-way stainless steel pipe cross was attached to the top of the reactor flange, shown in Figure 2 left, to allow hardware such as thermocouples to be inserted into the reactor. The cross also contains the gas inlet port for the reactor. The reactors fabricated utilize an Ultra-Torr fitting as the rotating seal, which is located at the top arm of the stainless steel cross. The fabricated carbon removal insert hardware utilized brass all-thread rods and brass stock for the stabilizing rings and funnel. Custom carbon steel brushes (Schaefer Brush) were used as the catalyst material for each reactor. These reactors were designed and built to be modular which will allow easy swapping of reaction subsystems and the testing of various interchangeable brushes with different geometries, densities, and materials. The total length of the assembled reactor is approximately 40 inches including the rotating shaft and exit tubing. Carbon capture is performed using a HEPA filter bag downstream and immediately after the reactor**.** The bag is contained in a polycarbonate vessel that allows gas products to exit. Although gravity assists in transporting the carbon into the filter bag in the lab, in microgravity gas flow would carry carbon particles into the filter bag as well.

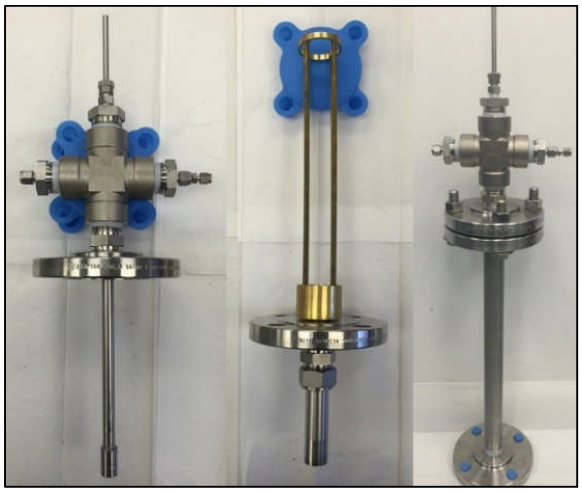

Figure 2. Reactor hardware (left and center) and completed reactor (right).

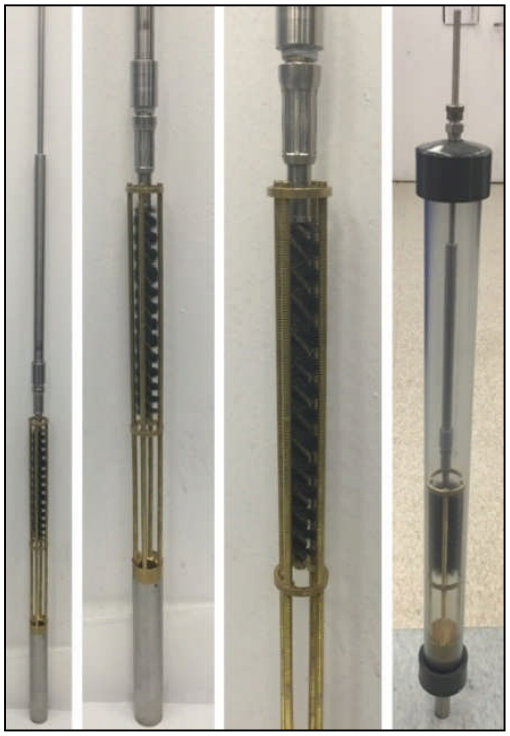

Figure 3. The catalytic brush inserted into the rod apparatus, and a clear PVC tube, far right, showing the confiugration inside the reactor.

The reaction conditions were as follows. The reactors were operated with two heating zones. The inlet of the reactor was heated to 600°C while the exit was at 500°C. This was done to promote faster kinetics at the inlet and better thermodynamic conversion at the exit. The reactor volume, catalyst mass, and gas flow rates are given in Table 1. The gas flow rates were set to give a nine-second residence time. The gas composition was taken to match previous experiments performed by others[7]. The addition of hydrogen helps the Boudouard reaction and makes the carbon formed more granular but also leads to the methanation of carbon monoxide, CO, via Equation 2. Carbon dioxide formed by the Boudouard reaction also reacts with hydrogen to make methane, Equation 3. A schematic of the sytem is shown in Figure 4.

Table 1. Parameters for each reactor.

	1-inch reactor	2-inch reactor
Reactor volume, cc	76	300
Catalyst mass, g	1.31	11.82
H_2 flow, sccm	232	909
CO flow, sccm	232	909
N_2 flow, sccm	52	202

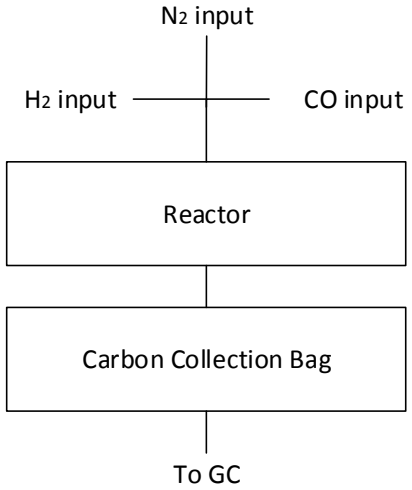

Figure 4. Schematic of Boudouard system

The gas products of the reaction were sampled by a Varian CP-4900 microGC. The volume percentages of carbon monoxide, carbon dioxide, hydrogen, and methane were taken every 5-6 minutes throughout the course of each test. The mass of solid carbon was measured after the test of the 1-inch reactor. It included carbon collected in the carbon capture bag and carbon removed from the reactor body after the test. For the 2-inch reactor, the mass of carbon captured in the collector was recorded periodically during the test.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (3)$$

B. Data Analysis

The yield of CO_2 and CH_4 and total carbon balance were calculated for each data point collected by the GC. Since the mole fraction, MF_i, of an ideal gas is proportional to the volume fraction, VF_i, the mole fraction for each product was calculated using the volume fractions of each gas, with the assumption that the number of moles of carbon dioxide equals the number of moles of solid carbon formed, Equation 4. The moles of carbon entering the reactor, CO_{in}, is the volumetric flow rate of carbon monoxide, VF_{CO}, multiplied by the time between GC samples, t, and divided by the number of liters of one mole of an ideal gas, 22.4, Equation 5. The moles of each carbon product exiting the reactor, Mol_i, is the mole fraction of each multiplied by the moles of CO entering the reactor, Equation 6. The yield, Equation 7, for the Boudouard and methanation reactions were calculated by dividing the moles of carbon dioxide or methane produced by the total amount that could be produced (n= 0.5 for Boudouard and 1 for methanation).

$$MF_i = \frac{VF_i}{VF_{CO} + 2 \times VF_{CO2} + VF_{CH4}} \quad (4)$$

$$CO_{in} = \frac{VF_{CO} \times t}{22.4} \quad (5)$$

$$Mol_i = MF_i \times CO_{in} \quad (6)$$

$$yield = \frac{Mol_i}{n \times CO_{in}} \quad (7)$$

III. Results and Discussion

A. 1-inch diameter reactor

The 1-inch diameter reactor was run twice: a 4-hour and an 8-hour session for a total of 12 hours. The reactor was not opened, nor was any carbon manually removed in between the two sessions. The gas composition exiting the reactor and the yield are given in Figure 5 and Figure 6. The gas concentrations continued to change throughout the 12 hours, indicating the reactor never reached steady state. It is unknown if the void spaces were completely filled at the end of 12 hours. The CO_2 yield increased during the test, reaching a maximum of 51% and averaging 40% over the duration of the run. The reactor also produced a small amount of methane. The methane yield also increased over the course of the reaction, reaching a maximum of 4.6% and an average of 3.1%.

A total of 20.5 g of solid carbon were collected from the 12 hours of operation. Assuming the molar amount of solid carbon formed is equal to the amount of carbon dioxide measured by the GC, there should have been 18.0 g of carbon. The values are in good agreement, and the discrepancy is likely due to propagation of errors between the flow controllers and measured GC values plus the carbon may have contained adsorbed water produced by Equations 2 and 3.

Of the total carbon, 5.5 g or 27% of the carbon was collected in the collection bag. The reactor has void space where carbon can build up and is not subjected to the carbon removal mechanism. It is likely that this void space needs to be filled before the carbon collection mechanism becomes completely effective. No attempt was made to measure the carbon captured in the bag in between the 4 and 8 hour runs, so it is not known if the rate of carbon capture in the bag changed over the course of the run.

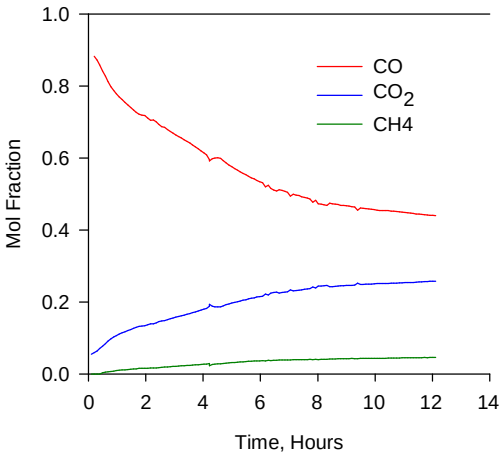

Figure 5. Mole fraction of gas exiting the 1 inch reactor.

After the 12 hours of test time, the reactor was opened to evaluate the state of the catalyst and cleaning mechanism. Unfortunately, the cleaning mechanism jammed and was damaged while the reactor was being opened, so the catalyst could not be evaluated. Whether the jam occurred during reactor opening or was a result of reactor operation could not be determined.

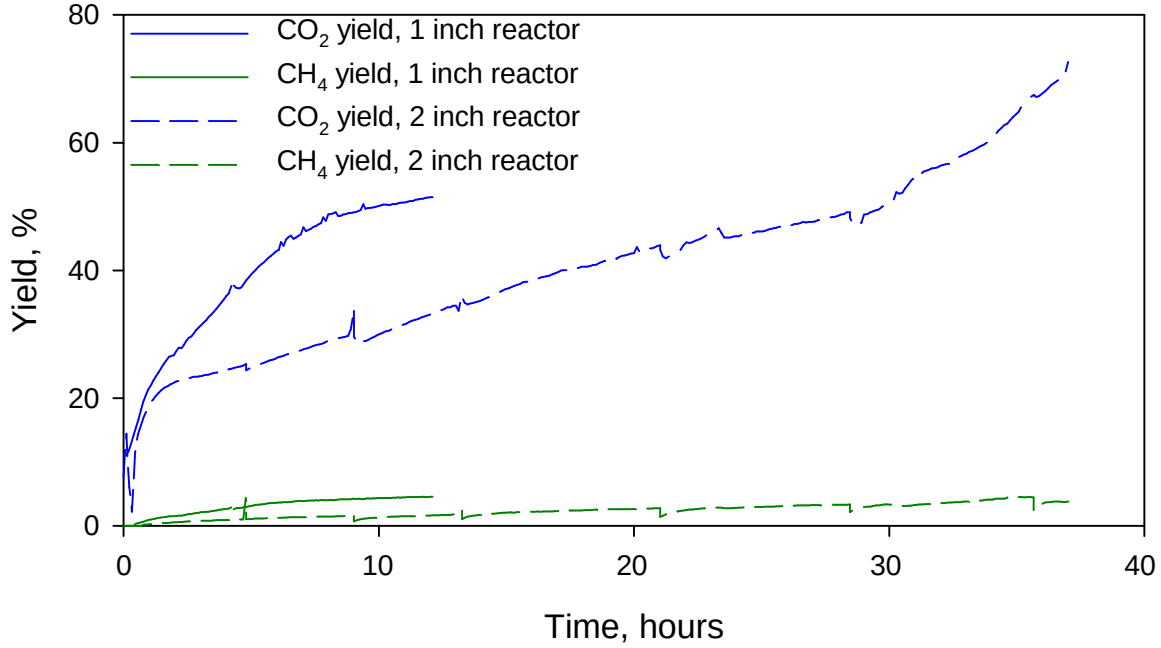

Figure 6. CO_2 and CH_4 yields for both reactors.

B. 2-inch diameter reactor

The 2-inch diameter reactor was run for approximately 37 hours in seven sessions. Near the end of 37 hours, a pressure increase in the reactor was observed and testing of the reactor was stopped to identify the problem.

The mole fractions of carbon containing gas in reactor effluent are shown in Figure 7. Similar to the 1-inch reactor, the mole fractions of each product changed over the entire time the reactor was run. The CO_2 yield, Figure 6, also continued to increase. The maximum CO_2 yield was 73% and the average over the entire run time was 41%. The maximum CH_4 yield was 3.8%, and the average was 2.3%.

The reactor operated normally until a small increase in the pressure inside the reactor was noted around hour 36. The increase was due to a clog in the reactor that started earlier in the process. The CO_2 yield increased linearly for the first 27 hours. After that time the yield increased at a higher rate, as would be expected if the pressure in the reactor increased. The reactor was x-rayed before disassembly to determine the failure point, Figure 8. The x-ray imaging showed that the wires holding the brush bristles in place had unravelled and broken at the point where they connected to the rotating shaft. It is not clear why the unravelling occurred, as the brush rotation was in the direction that should have prevented unravelling. The brush after failure is shown in Figure 9. The bristles had become tangled with each other, and the rods were bent and misshapen.

The amount of carbon produced was estimated from the GC data. This is compared to the amount that was collected in the carbon collection bag and the amount collected from the reactor after failure in Table 2. 87% of the estimated carbon produced was collected. However, 75% of this carbon remained in the reactor (not in the collection bag).

Table 2. Carbon collected from bag and reactor compared to estimate of carbon formed.

	Mass, g
Carbon collected in bag	47.6
Carbon collected from reactor after failure	147
Total carbon collected	194.6
Carbon formation estimated from GC data	224

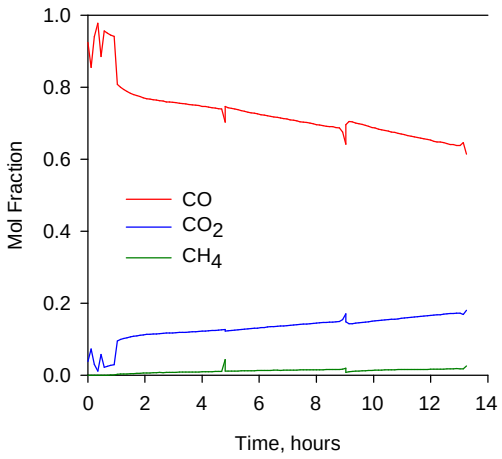

Figure 7. Mole fraction of gas exiting the 2 inch reactor.

Two scanning electron microscope images of the carbon collected from the two-inch reactor are shown in Figure 10. The left image is a secondary electron image and the right is a backscattered electron image. The right image gives contrast between elements with the brighter areas being a heavier element identified as iron with energy dispersive spectroscopy. The carbon formed in long filaments or ribbons. There were small particles of iron distributed throughout the carbon. The iron has two possible sources: the carbon steel brush or the stainless steel reactor wall. Since no nickel or chromium was detected, the source is likely the brush. This indicates that the brush catalyst would have a finite lifetime, even if the structure of the brush had not failed.

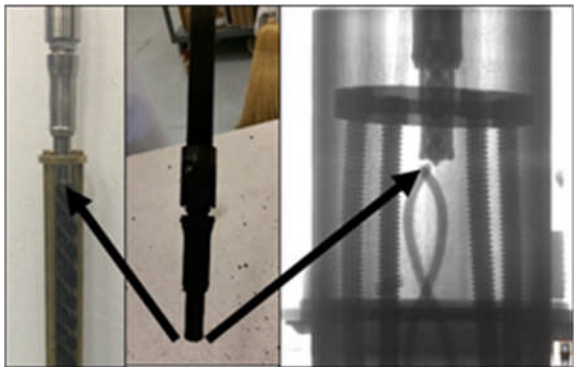

Figure 8. X-ray of reactor after failure, right, showing that the brush had unravelled and broken where it attached to the rotating mechanism, left.

Figure 9. Wide view, top, and close up, bottom, of brush from 2 inch reactor after failure.

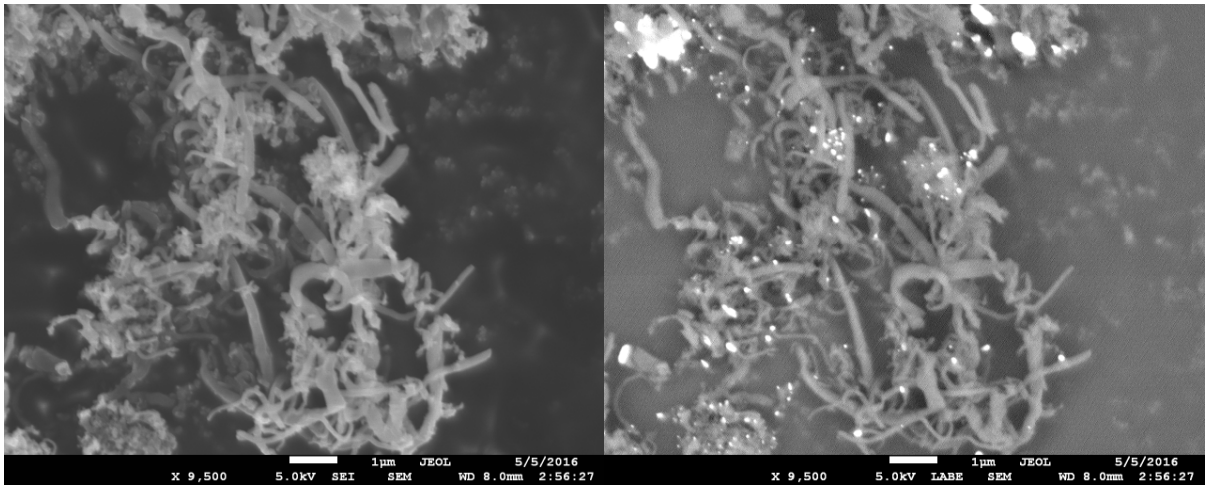

Figure 10. Secondary electron, left, and backscatter electron, right, images of carbon collected from the two inch reactor.

IV. Conclusions

The initial tests on this self-cleaning Boudouard reactor were promising and show that the concept of a self-cleaning Boudouard reactor is feasible. The yield of CO_2 continued to increase for the entire duration of tests with both the 1- and 2-inch diameter reactors and 25% of the carbon was recovered outside of the reactor. However, in both of the reactors the brush failed. The two-inch reactor produced 5 g/h of carbon, which converts to removal of 440 g CO_2 per day. This is 44% of the CO_2 exhaled by one crew member in a day. Iron from the brush catalyst was identified in the carbon and indicates that the catalytic brush bristles have a finite lifetime.

The failures of the brush cleaning mechanism were due to material failures of the brush. A second cleaning mechanism that uses more durable materials without brushes was designed and constructed. This mechanism is currently under evaluation in the two-inch reactor in our laboratories. The new mechanism minimizes the amount of mechanical connections and failure points and is expected to last much longer, greatly reducing the mass of consumables needed to recover oxygen from spacecraft CO_2 as well as significantly reducing the frequency of catalyst replacements for a Bosch-type spacecraft oxygen recovery system.

Acknowledgments

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